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PATENT
#01-0153-UNI
Case #J3568(C)

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Franklin et al.
Serial No.: 09/982,077
Filed: October 17, 2001
For: ESTERS

Edgewater, New Jersey 07020
December 3, 2001

SUBMISSION OF PRIORITY DOCUMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Pursuant to rule 55(b) of the Rules of Practice in Patent Cases, Applicant(s) is/are submitting herewith a certified copy of the Great Britain Application No. 0025437.5 filed October 17, 2000, upon which the claim for priority under 35 U.S.C. § 119 was made in the United States.

It is respectfully requested that the priority document be made part of the file history.

Respectfully submitted,

Kevin J. Stein
Reg. No. 47,966
Attorney for Applicant(s)

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The Patent Office
Concept House
Cardiff Road
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South Wales
NP10 8QQ

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Dated 29 August 2001

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Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference — **J3568 (C)/pmk**

2. Patent application number *(The Patent Office will fill in this part)* — 17 OCT 2000 **0025437.5**

3. Full name, address and postcode of the or of each applicant *(underline all surnames)* — **UNILEVER PLC**
UNILEVER HOUSE, BLACKFRIARS
LONDON, EC4P 4BQ

   Patents ADP number *(if you know it)* — 00001628002

   If the applicant is a corporate body, give the country/state of its incorporation — **UNITED KINGDOM**

4. Title of the invention — **ESTERS**

5. Name of your agent *(if you have one)* — **PEARCE, Timothy**

   "Address for Service" in the United Kingdom to which all correspondence should be sent *(including the postcode)* — **PATENT DEPARTMENT, UNILEVER PLC**
COLWORTH HOUSE, SHARNBROOK
BEDFORD, MK44 1LQ

   Patents ADP number *(if you know it)* — 07667579001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day/month/year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
   a) any applicant named in part 3 is not an inventor, or
   b) there is an inventor who is not named as an applicant, or
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Claim(s)	7
Abstract	1
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Priority Documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	1
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature(s) Date: **17/10/00**

Sandra EDWARDS, Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Petra Kimber, Tel 01234 222893

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Esters

The present invention relates to esters and in particular to esters of cellobiose, compositions containing them, and their use as structurants.

Background

Many compositions intended for topical application to skin, including a number for various parts of the body, such as face, gums, hands, limbs, feet, torso, underarm, breasts, genitalia, hair and other parts of the body, comprise one or more active agents are distributed within or otherwise supported by a carrier fluid. Although it is possible, in many instances, that such compositions are in the form of lotions, it is often desirable that the active ingredient in such compositions, be it for medical or for cosmetic purposes, remains substantially localised in the region of the body to which it has been topically applied. In order to assist this to happen and also to enable alternative dispensers for the composition to be employed, the carrier fluid can be thickened or structured, for example by introducing one or more materials for that purpose. Thickened or structured compositions commonly adopt the form of firm sticks, or soft solids and creams. In such circumstances, the materials are often referred to as structurants or gelants and may sometimes alternatively be called thickeners, depending on the final form of the composition. The carrier fluid may comprise water and/or a water-miscible organic liquid and alternatively or additionally a water-immiscible liquid.

In general, the choice of structurants or thickeners tends to vary in accordance with the physical nature of

the carrier fluid and in particular on whether it is water-miscible or immiscible. The present invention is directed more particularly towards materials which are capable of structuring a water-immiscible liquid, which may act by itself as carrier for an active ingredient or comprise a water-immiscible phase in an emulsion or micro-emulsion.

Many materials have been proposed for structuring or thickening a water-immiscible liquid phase of a composition intended for topical application to humans. These have included waxes natural waxes, such as paraffin waxes or those typically extracted from vegetation, such as candelilla wax, or glyceride waxes, or produced by chemical treatment of natural oils, for example hydrogenation of castor oil, or produced by extracted from fauna, such as beeswax or spermaceti wax, or derivatives or synthetic variants of them. Others include fatty alcohols, eg linear C18 or C22 alcohols. Other materials are polymeric, such as polysiloxane waxes, or polysiloxane elastomers, or various polyamide/polysiloxane copolymers.

In the closing years of the 20th century, a number of structurants were identified which the present inventors classify as fibre-forming. These include 12-hydroxy stearic acid, various amino acid amides, including particularly, combinations of sterols and sterol esters, including particularly β-sitosterol and γ-oryzonol, derivatives of threitol, diamide derivatives of cyclohexane, and acylated derivatives of cellobiose. Each of the various structurants has to a greater or lesser extent its particular benefits and its intrinsic disadvantages, either in absolute or relative terms. These properties can include the ability of the material to gel or otherwise structure the carrier liquid,

including the resultant hardness and stability, and the sensory properties and appearance of the resultant composition, the latter being of great importance for cosmetic compositions.

One of the most desirable class of structurants comprises acylated cellobiose, as described in pending PCT application No PCT/GB 00/01228, particularly for structuring a water-immiscible liquid in a cosmetic compositions, including especially antiperspirant and deodorant compositions. Said PCT application describes various benefits for the acylated cellobiose structurant and exemplifies many compositions demonstrating such benefits. In said PCT application, it has been disclosed that the cellobiose can adopt either an α or β configuration, preferably the former, and various preferences are given for both the number of acyl substituents of the cellobiose nucleus and the chemical constitution of the substituents. The description of alternatives included the choice of an aliphatic acyl substituent, whether it is linear or branched and its chain length. Acylated cellobiose materials were exemplified in which identical acyl substituents were employed. The most highly preferred acylated cellobiose described therein is cellobiose octanonanoate.

Continuing research into the properties of acylated cellobiose materials and compositions structured using them has shown that variations in the structurants can result in changes to various of the properties of the structured compositions, including amongst other things the thermal stability of the final structured material, the resistance of the structurant to crystallisation in situ, and the clarity and hardness of the composition.

α-cellobiose octanonanoate has been shown to be an extremely good structurant for water-immiscible liquids, including silicone fluids and water-immiscible emollient liquids employed in many cosmetic compositions. However, ongoing research into the acylated cellobiose structurants has indicated that its thermal stability could be improved and that long term storage can lead to a gradual reduction in clarity. This would appear from studies to be associated with crystallisation of the structurant. Either effect conveys self-evident disadvantages. Loss of structural strength with time limits the shelf life of the product and a reduction in clarity can be taken by consumers as a visual cue that efficacy has been impaired. Formulations like consumer formulations can take a long time to pass through conventional manufacture and distribution channels and can sometimes also spend a long time on consumers' shelves before or during use, so that it is desirable to find ways of ameliorating or overcoming any negative effects that would otherwise arise during storage. It will, of course, be recognised that any changes made should endeavour not to sacrifice any of the other beneficial properties of the products.

However, many compositions are desirably translucent or transparent and the controlled hardness of the composition remains an important characteristic. Consequently, any change made to the formulation or alternative selection made from the class of acylated cellobiose materials should endeavour to minimise or even overcome and reverse any impairment to the other properties of the structurant which might arise when seeking to improve one of the properties. By way of example, measures to improve stability against in situ crystallisation can reduce hardness. Mixtures of the materials can be contemplated and then some trade-off in

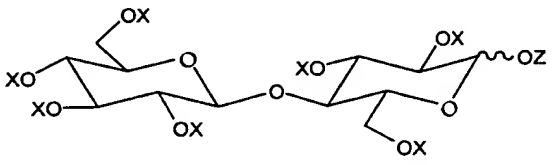
the performance of the structurant mixture compared with its constituents has been observed.

It is an object of the present invention to provide an alternative acylated cellobiose which demonstrates an attractive combination of properties, particularly in the context of acting as a structurant for a water-immiscible liquid.

It will be understood, however, that although the material of the instant invention is contemplated especially for use in cosmetic formulations, its potential use is much wider, including the structuring of a water-immiscible liquid to make a cream, soft solid or stick for any other purpose. Such other purposes could include topical medicaments, topically applied veterinary products or animal cosmetics and waxes or polishes.

Brief Description of the Invention

According to a first aspect of the present invention there is provided as a new compound, an acylated cellobiose satisfying the general formula:



in which X represents an acyl group (R-CO-) or H, Z represents an acyl group (R'-CO-) or H and not more than a minority of X + Z residues represent H,

R represents a saturated or unsaturated, linear or branched chain hydrocarbon residue containing from 5 to 31 carbon atoms and

R′ represents a residue which is different from R and which is :-

(i) a saturated or unsaturated, linear or branched chain hydrocarbon residue containing from 1 to 31 carbon atoms, optionally substituted or;

(ii) an aromatic hydrocarbon residue, optionally substituted or;

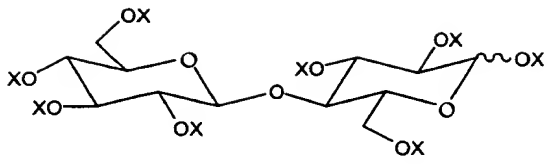
(iii) a cycloaliphatic hydrocarbon, optionally substituted.

The Z substituent is at the anomeric position.

Such materials demonstrate an excellent combination of properties rendering those materials particularly suitable for structuring or thickening water-immiscible liquids, enabling them to be employed in the manufacture of base gels for cosmetic or medical actives. The benefits accrue by selecting substitution R′ at the anomeric carbon which is different from that of the other alkyl groups R.

For example, by comparison with the employment of various cellobiose octaesters, advantageously, improvements in one or more of the following properties can be seen, namely clarity, thermal stability and resistance against in situ crystallisation, whilst not sacrificing hardness.

According to a second aspect of the present invention there is provided a method for the preparation of an acylated cellobiose as described in the first aspect hereinabove comprising the step of
reacting an acylated cellobiose having general formula 2



in which X represents an acyl group (R-CO-) or H, being not more than a minority of X residues and R represents a saturated or unsaturated, linear or branched chain hydrocarbon residue containing from 5 to 31 carbon atoms with an acylating agent containing a residue R' as described hereinabove preferentially at the anomeric carbon of the cellobiose.

In this aspect, either the hydroxyl group at the anomeric carbon atom is acylated, or the acyl group R-CO- at the anomeric carbon atom is transesterified.

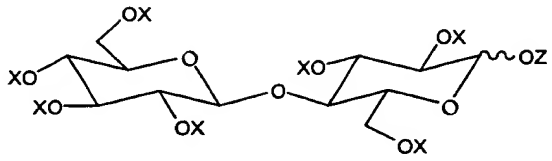
In a third aspect of the present invention there is provided the use of an acylated cellobiose as described in the first aspect hereinabove for thickening or structuring a water-immiscible liquid, thereby forming a cream, soft solid or solid.

In a fourth aspect of the present invention, there is provided a base composition in the form of a cream, soft solid or solid containing a structurant or thickener an acylated cellobiose as described hereinabove in the first aspect.

In a related fifth aspect of the present invention, the base composition of the fourth aspect additionally contains an active cosmetic, medical, or veterinary agent.

Detailed Description of the Invention and Preferred Embodiments

Herein the acylated cellobiose compounds satisfy the formula shown below:



When X and Z represent respectively -COR and -COR' in this formula, R represents a saturated or unsaturated, linear or branched chain hydrocarbon residue which contains from 5 to 31 carbon atoms, preferably from 7 and 12 carbon atoms and especially 8 or 9 carbon atoms. Preferably R residues are saturated and desirably are linear. Most desirably, all R groups are the same. It will be recognised that in practice the alkyl substituent of a specified chain length in an acylating agent can contain impurity levels of isomers or close homologues. For example, when R is nominally octyl, the substituent can comprise as impurities a low proportion, typically not more than 5% of iso octyl and n-heptyl /n-nonyl groups.

In this formula, R' represents an aliphatic, aromatic or cycloaliphatic residue. R' can be alkyl, alkaryl, aryl, or aralkyl, optionally substituted.

The aliphatic residue R' can comprise a saturated or unsaturated, linear or branched chain hydrocarbon residue containing from 1 to 31 carbon atoms, and preferably from 2 to 22 carbon atoms. The R and R' residues are different from each other, so that R' is often selected in the ranges of from less than 2 carbons or greater than

2 carbons than R, and conveniently in the ranges of from 1 to 6 and 13 to 22 carbon atoms. Particularly desirable short chain alkyl R' residues include methyl, ethyl, and propyl. The alkyl groups within R' can optionally he fluorinated or substituted by an aryl group such as those described hereinafter.

When R' represents or contains an aromatic hydrocarbon residue, particularly an aryl residue, suitable examples comprise phenyl, naphthyl and biphenyl residues. The aryl group can comprise 1 or a plurality of nuclei, which may be fused or not fused. The aryl nucleus or nuclei therein can be substituted, for example by an alkyl or alkoxy group containing up to 20 carbon atoms or a halo group such as fluoro or a nitro group.

When R' represents a cycloaliphatic hydrocarbon residue, suitable examples include cyclohexane and cyclooctane. The cycloaliphatic nuclei can be substituted for example by an alkyl group containing up to 20 carbon atoms or by an aryl group such as described above.

R' can comprise an alkyl, aryl, cycloalkyl, alkaryl, aralkyl or cycloalkylaryl residue.

The acylated cellobiose materials according to the present invention can adopt either of the α and β anomeric forms or mixtures thereof.

Preferably, the acylated cellobiose is acylated by greater than seven acyl substituents, R-CO- + R'-CO-, on average, and especially by at least 95 molar % of total acylation. In practice, we have found that acylation

occurs preferentially at cellobiose carbons other than at its anomeric carbon atom, so that the former carbons tend to be fully acylated whilst anomeric carbon is acylated to a lesser proportion. It is desirable that the anomeric carbon is acylated to at least 50% and preferably is at least 75% acylated, and most desirably in conjunction with X representing at or substantially 100% R-CO- (normally greater than 97%).

The acylated cellobiose materials of the present invention may be used as a sole or primary structurants or may be used as minor or supplementary structurant in conjunction with one or more of the classes of structurants that are mentioned hereinafter. By way of example, the invention structurants can be used together with an acylated cellobiose described in PCT/GB 00/01228, in which the anomeric acyl group is the same as at least some of the other acyl groups, ie R = R', such as cellobiose octanonanoate.

It is especially desirable to employ acylated cellobiose materials identified herein in which all the R substituents are identical and are n-nonyl or particularly n-octyl and at least 75% of substituents at the anomeric carbon are R' = cyclohexyl, phenyl, naphthyl or methyl.

Material Preparation

One convenient and general method for making the acylated cellobiose compounds of the present invention comprises the step of transesterifying a corresponding acylated cellobiose in which the acyl substituents -COR and -COR' are identical. Such a process in practice can be two

step, in the first step of which comprises preparing an octaesterified cellobiose, for example by a process as described hereinbelow. The second step of such a process comprises reacting the octaester with an acylating agent containing a -COR' residue, capable of displacing the residue -COR, if needed in the presence of a strong acylating catalyst. The resultant product often comprises a proportion of residual R-CO- residues at the anomeric carbon atom.

A related method comprises acylating the corresponding partially acylated cellobiose with an acylating agent containing a -COR' residue, where needed in the presence of an acylating catalyst, the anomeric carbon being partly or preferably wholly or substantially wholly substituted by an hydroxyl group. Such a substrate can be obtained, for example, by deacylating wholly or partly a cellobiose octester Consequently, the invention mixed ester cellobiose compounds can be made in a three step process comprising the steps of first making an octaester in which the acyl substituent -COR' at the anomeric carbon is the same as at the other cellobiose carbons, R-CO-, secondly removing the anomeric acyl substituent, and then re-acylating at the anomeric position with a different acyl substituent.

In one way of carrying out the first step, be it for either the two or three step processes indicated above, cellobiose (commonly D-+-cellobiose) is reacted with a molar excess of an acylating agent, often substantial, such as an acid chloride, RCOCl, carboxylic acid RCO_2H or acid anhydride $(RCO)_2O$ and, where necessary, an acylation catalyst. The R groups are as hereinbefore described. For example, when using an acid as acylating agent, the catalyst can desirably be derivable from an acid having a

low pK_a such as an anhydride $(R''CO)_2O$, often in a significant molar excess. The R" group is desirably a polychlorinated or preferably polyfluorinated alkyl, such as trifluoromethyl. The acylating agent, eg carboxylic acid, is preferably employed at a mole ratio to the cellobiose in the range of at least 50:1 and especially from 60:1 to 100:1. The catalyst is preferably employed with the acid at a mole ratio to the cellobiose of at least 20:1 and particularly from 22:1 to 50:1. The acylation is desirably conducted at an elevated temperature such as above 70°C and especially approximately 100°C for a period of at least 2 hours and especially from 3 to 10 hours. The resultant product is substantially or completely acylated, that is to say that at least 90% of the acylatable hydroxyl groups on the cellobiose have been acylated and often at least 95% acylated.

In the second step in the above-mentioned three step process, the acylated cellobiose produced in the first step is partially de-acylated preferentially at the anomeric carbon. One method comprises reacting the fully acylated cellobiose with a mixture of a low molecular weight aliphatic acid, (C1-C4) and especially acetic acid with an alkylene diamine such as in particular ethylene diamine, at a low concentration in THF (tetrahydrofuran), such as from 4 to 15% by weight acylated cellobiose. The acid employed in the second step has a higher pK_a than the catalyst in the first step. The reaction preferably employs an approximately equimolar ratio of acid to acylated cellobiose, such as in the range of 0.9 to 1.2:1 and a small molar excess of diamine to acylated cellobiose, such as from 1.6 to 2.5:1. The reaction can conveniently be carried out in at or about ambient temperature, eg 20 to 30°C for a long reaction time, often

of at least 12 hours and particularly from 24 to 60 hours. The resultant partially deacylated material can be recovered by extraction into a haloalkane solvent such as dichloromethane and acid washed. After drying, it is recrystallisable from a THF/methanol mixture.

In the third step, the partially de-acylated cellobiose is re-acylated. The re-acylation can employ a carboxylic acid, an acid chloride, or an anhydride.

In the first variant of this third step, the cellobiose is reacted with an at least equimolar amount of an acid chloride of formula R'COCl, preferably a small molar excess of from 1.1 to 1.5:1, in the presence of at least an equimolar amount of triethylamine and preferably a small molar excess of from 1.1 to 1.5:1. The reaction is desirably conducted at or within 10°C of reflux temperature, suitably for at least 1 hour and preferably from 2 to 4 hours.

In the second variant of this third step, the partially de-acylated cellobiose is reacted with an substantial excess of a carboxylic acid of formula $R'CO_2H$, such as a mole ratio of at least 50:1 and particularly from 60 to 100:1 in the presence of a significant molar excess of a strong acid catalyst such as that employed in the first step and preferably in a mole ratio to the cellobiose of at least 20:1 and especially from 22:1 to 50:1. The reaction is preferably carried out at elevated temperature, such as especially above 90°C and particularly at about 100°C. The reaction period is desirably at least 4 hours and is especially from 5 to 10 hours.

In the third variant for carrying out the third step, the partially-deacylated cellobiose is reacted with an

anhydride of formula $(R'CO)_2O$. The reaction is conveniently carried out in a hydrocarbon solvent having a boiling point of at least 80°C, such as toluene. The reaction preferably employs an excess anhydride, especially in a mole ratio to the cellobiose of at least 2:1, and often from 2.5 to 10:1.

Water-immiscible liquid

The water-immiscible liquid, which in many embodiments acts as a carrier for a disperse solid or liquid phase, normally comprises one or a mixture of materials which are relatively hydrophobic so as to be immiscible in water. Some hydrophilic liquid may be included in the water-immiscible liquid, to the extent that it is soluble or miscible with the water-immiscible liquid and provided the overall carrier liquid mixture is still immiscible with water. It will generally be desired that this carrier is liquid (in the absence of structurant) at temperatures of 15°C and above. It may have some volatility but its vapour pressure will generally be less than 4kPa (30 mmHg) at 25°C so that the material can be referred to as an oil or mixture of oils. More specifically, it is desirable in some embodiments, that at least 80% by weight of the hydrophobic carrier liquid should consist of materials with a vapour pressure not over this value of 4kPa at 25°C.

It is preferred, eg for use in cosmetic formulations that the hydrophobic carrier material includes a volatile liquid silicone, i.e. liquid polyorganosiloxane. To class as "volatile" such material should have a measurable vapour pressure at 20 or 25°C. Typically the vapour pressure of a volatile silicone lies in a range from 1 or 10 Pa to 2 kPa at 25°C.

It is desirable to include volatile silicone because it gives a "drier" feel to the applied film after the composition is applied to skin.

Volatile polyorganosiloxanes can be linear or cyclic or mixtures thereof. Preferred cyclic siloxanes include polydimethylsiloxanes and particularly those containing from 3 to 9 silicon atoms and preferably not more than 7 silicon atoms and most preferably from 4 to 6 silicon atoms, otherwise often referred to as cyclomethicones. Preferred linear siloxanes include polydimethylsiloxanes containing from 3 to 9 silicon atoms. The volatile siloxanes normally by themselves exhibit viscosities of below 10^{-5} m^2/sec (10 centistokes), and particularly above 10^{-7} m^2/sec (0.1 centistokes), the linear siloxanes normally exhibiting a viscosity of below 5 x 10^{-6} m^2/sec (5 centistokes). The volatile silicones can also comprise branched linear or cyclic siloxanes such as the aforementioned linear or cyclic siloxanes substituted by one or more pendant $-O-Si(CH_3)_3$ groups. Examples of commercially available silicone oils include oils having grade designations 344, 345, 244, 245 and 246 from Dow Corning Corporation; Silicone 7207 and Silicone 7158 from Union Carbide Corporation; and SF1202 from General Electric.

The hydrophobic water-immiscible liquid carrier employed in many compositions herein can alternatively or additionally comprise non-volatile silicone oils, which include polyalkyl siloxanes, polyalkylaryl siloxanes and polyethersiloxane copolymers. These can suitably be selected from dimethicone and dimethicone copolyols. Commercially available non-volatile silicone oils include Dow Corning 556 and Dow Corning 200 series.

The water-immiscible liquid carrier may contain from 0 to 100% by weight of one or more liquid silicones. Some embodiments contain liquid silicones in at least 10%, better at least 15%, by weight of the whole composition. If silicone oil is used, volatile silicone preferably constitutes from 10 to 100% of the weight of the carrier liquid. In many instances, when a non-volatile silicone oil is present, its weight ratio to volatile silicone oil is chosen in the range of from 1:3 to 1:40. In other embodiments, liquid silicones are absent, or present in only a small proportion of the water-immiscible phase, such as up to 7 or 8% by weight.

Silicon-free hydrophobic liquids can be used instead of, or in some embodiments in addition to liquid silicones. Silicon-free hydrophobic organic liquids which can be incorporated include volatile or non-volatile liquid aliphatic hydrocarbons such as mineral oils or hydrogenated polyisobutene, often selected to exhibit a low viscosity. Further examples of liquid hydrocarbons are polydecene and paraffins and isoparaffins of at least 10 carbon atoms.

Other hydrophobic carriers are liquid aliphatic or aromatic esters, but for some uses, for example antiperspirant formulations, these should be used as only part of the liquid carrier, desirably not above 20%, and possibly less than 10% by weight of the water-immiscible liquid carrier.

Suitable aliphatic esters contain at least one long chain alkyl group, such as esters derived from C_1 to C_{20} alkanols esterified with a C_8 to C_{22} alkanoic acid or C_6 to C_{10} alkanedioic acid. The alkanol and acid moieties or mixtures thereof are preferably selected such that they each have a melting point of below 20°C. These esters

include isopropyl myristate, lauryl myristate, isopropyl palmitate, diisopropyl sebacate and diisopropyl adipate.

Suitable liquid aromatic esters, preferably having a melting point of below 20°C, include fatty alkyl benzoates. Examples of such esters include suitable C_8 to C_{18} alkyl benzoates or mixtures thereof.

Further instances of suitable hydrophobic carriers comprise liquid aliphatic ethers derived from at least one fatty alcohol, such as myristyl ether derivatives e.g. PPG-3 myristyl ether or lower alkyl ethers of polygylcols such as nominally PPG-14 butyl ether.

Aliphatic alcohols which are solid at 20°C, such as stearyl alcohol are preferably absent or present in low concentration such as less than 5% by weight of the whole composition since these lead to visible white deposits when a composition is used.

However, aliphatic alcohols which are liquid at 20°C may be employed. These include branched chain alcohols of at least 10 carbon atoms such as isostearyl alcohol and octyl dodecanol.

Silicon-free liquids can constitute from 0-100% of the water-immiscible liquid carrier. It is preferred that silicone oil and/or a hydrocarbon oil is present and that the total amount of other liquid carriers preferably constitutes up to 50 or 60% for example from 0 to 10% OR 10 to 20% by weight of the water-immiscible carrier liquid.

An especially desired combination of water immiscible carrier liquids comprises a mixture of a silicone liquid such as a cyclomethicone and a hydrocarbon liquid, such

as in a weight ratio of the former to the latter of from 3:2 to 1:10, optionally in the presence of an emollient water-immiscible liquid.

Emulsion

Many formulations according to the present invention also contain a more polar disperse phase. In such compositions, the invention acylated cellobiose acts as a structurant in the continuous water-immiscible phase. The disperse phase may be a polar liquid alone or conveniently comprise a solution of an active ingredient, such as an antiperspirant salt.

The hydrophilic disperse phase in an emulsion normally comprises water as solvent and can comprise one or more water-soluble or water-miscible liquids in addition to or as a replacement for water. The proportion of hydrophilic carrier fluid, eg water, in the disperse phase, in an emulsion according to the present invention is often selected in the range of up to 60%, and particularly from 10% up to 40% or 50% of the whole formulation.

One class of water-soluble or water-miscible liquids comprises short chain monohydric alcohols, e.g. C_1 to C_4 and especially ethanol or isopropanol, which can impart a deodorising capability to the formulation. A further class of hydrophilic liquids comprises diols or polyols preferably having a melting point of below 40°C, or which are water miscible. Examples of water-soluble or water-miscible liquids with at least one free hydroxyl group include ethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, 2-ethoxyethanol, diethylene glycol monomethylether, triethyleneglycol monomethylether and

sorbitol. Especially preferred are propylene glycol and glycerol.

In an emulsion the disperse phase is likely to constitute from 5 to 80 or 85% of the weight of the composition preferably from 5 to 50 or 65% more preferably from 25 or 35% up to 50 or 65%, while the continuous phase with the structurant therein provides the balance from 15 or 35% up to 95% of the weight of the composition. Advantages can accrue when the internal phase volume constitutes a minor proportion of emulsion, such as from about 30 to 45% by weight. Yet other advantages arise at 45 to 65% internal phase volume. Compositions with high proportion of disperse phase, i.e. from 65 to 85% disperse phase, may also be advantageous. They can give good hardness even though the concentration of esterified saccharide structurant may be only a small percentage of the total composition.

An emulsion composition will generally include one or more emulsifying surfactants which may be anionic, cationic, zwitterionic and/or nonionic surfactants. The proportion of emulsifier in the composition is often selected in the range up to 10% by weight and in many instances from 0.1 or 0.25 up to 5% by weight of the composition. Most preferred is an amount from 0.1 or 0.25 up to 2 or 3% by weight. Nonionic emulsifiers are frequently classified by HLB value. It is desirable to use an emulsifier or a mixture of emulsifiers with an overall HLB value in a range from 2 to 10 preferably from 3 to 8.

It may be convenient to use a combination of two or more emulsifiers which have different HLB values above and below the desired value. By employing the two emulsifiers together in appropriate ratio, it is readily

feasible to attain a weighted average HLB value that promotes the formation of an emulsion.

Many suitable emulsifiers of high HLB are nonionic ester or ether emulsifiers comprising a polyoxyalkylene moiety, especially a polyoxyethylene moiety, often containing from about 2 to 80, and especially 5 to 60 oxyethylene units, and/or contain a polyhydroxy compound such as glycerol or sorbitol or other alditol as hydrophilic moiety. The hydrophilic moiety can contain polyoxypropylene. The emulsifiers additionally contain a hydrophobic alkyl, alkenyl or aralkyl moiety, normally containing from about 8 to 50 carbons and particularly from 10 to 30 carbons. The hydrophobic moiety can be either linear or branched and is often saturated, though it can be unsaturated, and is optionally fluorinated. The hydrophobic moiety can comprise a mixture of chain lengths, for example those deriving from tallow, lard, palm oil, sunflower seed oil or soya bean oil. Such nonionic surfactants can also be derived from a polyhydroxy compound such as glycerol or sorbitol or other alditols. Examples of emulsifiers include ceteareth-10 to -25, ceteth-10-25, steareth-10-25 (i.e. C_{16} to C_{18} alcohols ethoxylated with 10 to 25 ethylene oxide residues) and PEG-15-25 stearate or distearate. Other suitable examples include C_{10}-C_{20} fatty acid mono, di or tri-glycerides. Further examples include C_{18}-C_{22} fatty alcohol ethers of polyethylene oxides (8 to 12 EO).

Examples of emulsifiers, which typically have a low HLB value, often a value from 2 to 6 are fatty acid mono or possibly diesters of polyhydric alcohols such as glycerol, sorbitol, erythritol or trimethylolpropane. The fatty acyl moiety is often from C_{14} to C_{22} and is saturated in many instances, including cetyl, stearyl, arachidyl and behenyl. Examples include monoglycerides

of palmitic or stearic acid, sorbitol mono or diesters of myristic, palmitic or stearic acid, and trimethylolpropane monoesters of stearic acid.

A particularly desirable class of emulsifiers comprises dimethicone copolymers, namely polyoxyalkylene modified dimethylpolysiloxanes. The polyoxyalkylene group is often a polyoxyethylene (POE) or polyoxypropylene (POP) or a copolymer of POE and POP. The copolymers often terminate in C_1 to C_{12} alkyl groups. An especially desirable example of this class is available under the trade name ABIL EM90 for use within the aforementioned ranges of proportions.

Suitable emulsifiers and co-emulsifiers are widely available under many trade names and designations including Abil™, Arlacel™, Brij ™, Cremophor™, Dehydrol™, Dehymuls™, Emerest ™, Lameform™, Pluronic™, Prisorine™, Quest PGPR™, Span ™, Tween ™, SF1228, DC3225C and Q2-5200.

Antiperspirant Actives

If the composition is an antiperspirant, it will contain an antiperspirant active. Antiperspirant actives, are preferably incorporated in an amount of from 0.5-60%, particularly from 5 to 30% or 40% and especially from 5 or 10% to 30 or 35% of the weight of the composition.

Antiperspirant actives for use herein are often selected from astringent active salts, including in particular aluminium, zirconium and mixed aluminium/zirconium salts, including both inorganic salts, salts with organic anions and complexes. Preferred astringent salts include aluminium, zirconium and aluminium/zirconium halides and halohydrate salts, such as chlorohydrates.

Aluminium halohydrates are usually defined by the general formula $Al_2(OH)_xQ_y.wH_2O$ in which Q represents chlorine, bromine or iodine, x is variable from 2 to 5 and x + y = 6 while wH_2O represents a variable amount of hydration. Especially effective aluminium halohydrate salts, known as activated aluminium chlorohydrates, are described in EP-A-6739 (Unilever NV et al), the contents of which specification is incorporated herein by reference. Some activated salts do not retain their enhanced activity in the presence of water but are useful in substantially anhydrous formulations, i.e. formulations which do not contain a distinct aqueous phase.

Zirconium actives can usually be represented by the empirical general formula: $ZrO(OH)_{2n-nz}B_z.wH_2O$ in which z is a variable in the range of from 0.9 to 2.0 so that the value 2n-nz is zero or positive, n is the valency of B, and B is selected from the group consisting of chloride, other halide, sulphamate, sulphate and mixtures thereof. Possible hydration to a variable extent is represented by wH20. Preferable is that B represents chloride and the variable z lies in the range from 1.5 to 1.87. In practice, such zirconium salts are usually not employed by themselves, but as a component of a combined aluminium and zirconium-based antiperspirant.

The above aluminium and zirconium salts may have co-ordinated and/or bound water in various quantities and/or may be present as polymeric species, mixtures or complexes. In particular, zirconium hydroxy salts often represent a range of salts having various amounts of the hydroxy group. Zirconium aluminium chlorohydrate may be particularly preferred.

Antiperspirant complexes based on the above-mentioned astringent aluminium and/or zirconium salts can be

employed. The complex often employs a compound with a carboxylate group, and advantageously this is an amino acid. Examples of suitable amino acids include dl-tryptophan, dl-β-phenylalanine, dl-valine, dl-methionine and β-alanine, and preferably glycine which has the formula $CH_3CH(NH_2)CO_2H$.

It is highly desirable to employ complexes of a combination of aluminium halohydrates and zirconium chlorohydrates together with amino acids such as glycine, which are disclosed in US-A-3792068 (Luedders et al). Certain of those Al/Zr complexes are commonly called ZAG in the literature. ZAG actives generally contain aluminium, zirconium and chloride with an Al/Zr ratio in a range from 2 to 10, especially 2 to 6, an Al/Cl ratio from 2.1 to 0.9 and a variable amount of glycine. Actives of this preferred type are available from Westwood, from Summit and from Reheis.

Other actives which may be utilised include astringent titanium salts, for example those described in GB 2299506A.

The proportion of solid antiperspirant salt in a composition normally includes the weight of any water of hydration and any complexing agent that may also be present in the solid active. However, when the active salt is in solution, its weight excludes any water present.

If the composition is in the form of an emulsion the antiperspirant active will be dissolved in the disperse phase. In this case, the antiperspirant active will often provide from 3 to 60% by weight of the aqueous disperse phase, particularly from 10% or 20% up to 55% or 60% of that phase.

Alternatively, the composition may take the form of a suspension in which antiperspirant active in particulate form is suspended in the water-immiscible liquid carrier. Such a composition will probably not have any separate aqueous phase present and may conveniently be referred to as "substantially anhydrous" although it should be understood that some water may be present bound to the antiperspirant active or as a small amount of solute within the water-immiscible liquid phase. In such compositions, the particle size of the antiperspirant salts often falls within the range of 0.1 to 200 μm with a mean particle size often from 3 to 20μm. Both larger and smaller mean particle sizes can also be contemplated such as from 20 to 50μm or 0.1 to 3μm.

Optional ingredients

Optional ingredients in compositions of this invention can include deodorants, for example at a concentration of up to about 10% w/w. Suitable deodorant actives can comprise deodorant effective concentrations of antiperspirant metal salts, deoperfumes, and/or microbicides, including particularly bactericides, such as chlorinated aromatics, including biguanide derivatives, of which materials known as triclosan eg Igasan DP300 ™, Tricloban ™, and Chlorhexidine warrant specific mention. A yet another class comprises biguanide salts such as those available under the trade mark Cosmosil ™.

Other optional ingredients include wash-off agents, often present in an amount of up to 10% w/w to assist in the removal of the formulation from skin or clothing. Such wash-off agents are typically nonionic surfactants such as esters or ethers containing a C_8 to C_{22} alkyl moiety

and a hydrophilic moiety which can comprise a polyoxyalkylene group (POE or POP) and/or a polyol.

The compositions herein can incorporate one or more cosmetic adjuncts conventionally contemplatable for antiperspirant solids or soft solids. Such cosmetic adjuncts can include skin feel improvers, such as talc or finely divided polyethylene, for example in an amount of up to about 10%; skin benefit agents such as allantoin or lipids, for example in an amount of up to 5%; colours; skin cooling agents other than the already mentioned alcohols, such a menthol and menthol derivatives, often in an amount of up to 2%, all of these percentages being by weight of the composition. A commonly employed adjunct is a perfume, which is normally present at a concentration of from 0 to 4% and in many formulations from 0.25 to 2% by weight of the composition.

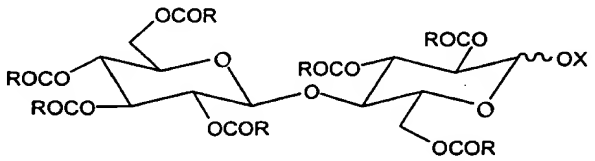
A further optional constituent of the formulation comprises one or more secondary structurants which can be employed in addition to the esterified saccharide of the present invention. The amount of such secondary structurants in the formulation is often zero, and usually not more than 15% of the formulation. In many embodiments, it is normally not greater than the amount of the primary structurant.

The secondary structurants employable herein can be non-polymeric or polymeric. Solid linear fatty alcohol and/or a wax may be included but are not preferred. Non-polymeric structurants, sometimes referred to as gellants, can be selected from fatty acids or salts thereof, such as stearic acid or sodium stearate or 12-hydroxy stearic acid. Other suitable gellants can comprise dibenzylidene alditols, e.g. dibenzylidene sorbitol. Further suitable gellants can comprise lanosterol, selected N-acyl amino acid derivatives,

including ester and amide derivatives, such as N-lauroyl glutamic acid dibutylamide, which gellants can be contemplated in conjunction with 12-hydroxy stearic acid or an ester or amide derivative thereof. Still further gellants include amide derivatives of di or tribasic carboxylic acids, such as alkyl N,N' dialkylsuccinamides, e.g. dodecyl N,N'-dibutylsuccinamide.

Polymeric structurants which can be employed can comprise organo polysiloxane elastomers such as reaction products of a vinyl terminated polysiloxane and a cross linking agent or alkyl or alkyl polyoxyalkylene-terminated poly (methyl substituted) or poly (phenyl substituted) siloxanes. A number of polyamides have also been disclosed as structurants for hydrophobic liquids. Polymers containing both siloxane and hydrogen bonding groups, which might be used as secondary structurants, have been disclosed in WO 97/36572 and WO 99/06473. If an aqueous disperse phase is present, polyacrylamides, polyacrylates or polyalkylene oxides may be used to structure or thicken this aqueous phase.

One especially desirable secondary structurant comprises an esterified cellobiose as described in PCT/GB 00/01228, which description is incorporated herein. Such a structurant is sometimes called an ACB structurant herein. Preferably the ACB structurant can be represented by the formula:-



in which R is as defined hereinabove in respect of the invention structurants and X represents either hydroxyl or an acyl group R-CO-. More preferably, the acyl group -COR is at least 50% and especially at least 75% of X.

In such ACB structurants, the alkyl group R is preferably octyl or nonyl or preferably may comprise mixtures of R groups having up to 2 fewer or 2 more carbons than an average of 8 to 9 carbons. The substituent -OX is present at the anomeric carbon in the cellobiose. the ACB structurant can be made in either α or β anomers. Highly desirably, the proportion of α anomer in the ACB structurant is greater than 50%, particularly greater than 80% and especially greater than 90%.

Herein, the ACB structurant can be employed advantageously with the primary invention structurant in a wide ratio of amounts, such as in a weight ratio thereto of up to 25:1, and in many instances up to 15:1, and in the same or other embodiments in the range of from 1:25, or sometimes from 1:5 or from 1:1. A convenient weight ratio of ACB to primary structurant is from 5:1 to 12:1.

Translucent/Transparent Compositions

When a composition of this invention is formulated as an emulsion it is possible to construct the formulation such that the emulsion is translucent or transparent. In order to do this the refractive indices of the water-immiscible continuous phase and the polar or aqueous disperse phase must be matched to each other and the value of refractive index at which they are matched must also approximately match the refractive index of the structurant.

The refractive index of a fibrous network of a structurant can be determined by using that structurant to gel a number of oils or oil mixtures of differing refractive index. The invention acylated cellobiose

fibrous networks have a refractive index which falls in a range between 1.45 and 1.51 at 22°C.

For the continuous phase, silicon-free water-immiscible liquid oils generally have refractive indices in a range from 1.43 to 1.49 at 22°C and can be used alone or mixed together to give a silicon-free carrier liquid with refractive index in this range. Volatile silicone oils generally have a refractive index slightly below 1.40 at 22°C, but carrier liquid mixtures with refractive indices in the range from 1.41 to 1.46 can be obtained by mixing volatile silicone with other oils. Non-volatile silicone oils generally have refractive indices in a range from 1.45 to 1.48 at 22°C and so can be included when desired.

The RI of the structured continuous phase will be very close to the RI of the carrier liquid (usually a carrier liquid mixture) which is its principal component.

For the disperse phase, a solution of an antiperspirant active salt in water alone will generally display a refractive index below 1.425. The refractive index can be raised by incorporating a diol or polyol into the aqueous solution. It is believed to be novel to match the refractive index of a polar disperse phase to that of a structurant network within a continuous phase. Moreover, it can be achieved without using so much diol or polyol as will make the composition excessively sticky.

Mechanical Properties and Product Packages

The compositions of this invention are structured liquids and may be firm or soft in appearance. Even a soft solid has an ability to sustain its own shape, for instance if it is removed from a mould without being subjected to

shear it will retain its shape for at least 30 seconds, usually longer.

A composition of this invention will usually be marketed as a product comprising a container with a quantity of the composition therein, where the container has at least one aperture for the delivery of composition, and means for urging the composition in the container towards the delivery aperture. Conventional containers take the form of a barrel of oval cross section with the delivery aperture(s) at one end of the barrel.

A composition of this invention may be sufficiently rigid that it is not apparently deformable by hand pressure and is suitable for use as a stick product in which a quantity of the composition in the form of a stick is accommodated within a container barrel having an open end at which an end portion of the stick of composition is exposed for use. The opposite end of the barrel is closed.

Generally the container will include a cap for its open end and a component part which is sometimes referred to as an elevator or piston fitting within the barrel and capable of relative axial movement along it. The stick of composition is accommodated in the barrel between the piston and the open end of the barrel. The piston is used to urge the stick of composition along the barrel. The piston and stick of composition may be moved axially along the barrel by manual pressure on the underside of the piston using a finger or rod inserted within the barrel. Another possibility is that a rod attached to the piston projects through a slot or slots in the barrel and is used to move the piston and stick. Preferably the container also includes a transport mechanism for moving the piston comprising a threaded rod which extends axially into the stick through a correspondingly threaded aperture in the piston, and means mounted on the barrel for rotating the rod. Conveniently the rod is rotated by

means of a hand-wheel mounted on the barrel at its closed end, i.e. the opposite end to the delivery opening.

If a composition of this invention is softer, but still capable of sustaining its own shape it will be more suited for dispensing from a barrel with a closure instead of an open end, where the closure has one or more apertures through which composition from the barrel can be extruded. The number and design of such apertures is at the discretion of the designer of the package.

The component parts of such containers are often made from thermoplastic materials, for example polypropylene or polyethylene. Descriptions of suitable containers, some of which include further features, are found in US patents 4865231, 5000356 and 5573341.

Having described the invention in general terms. specific embodiments thereof will be described more fully by way of example only.

Example 1

In this Example, cellobiose heptanonanoate ester compounds according to the present invention and summarised in table 1 below were made in a three step route, the first two steps of which was common to all variants and the third step of which was carried out by one of three routes. The route is exemplified for cellobiose heptanonoate esters. Other acylated cellobiose esters were made by substituting the same molar amounts of alternative acylating agents for nonanoic acid.

Step 1, Preparation of cellobiose octanonanoate

Cellobiose was esterified with nonanoic acid to yield the fully esterified product in the form of its α-anomer

following a procedure generally as described in Takada et al, Liquid Crystals, Volume 19, page 441 (1995).

The following materials, obtained from Acros Organics - Fisher Scientific, were used:
D-+-cellobiose, 20 grams, 0.058 moles
Nonanoic acid, 591.6 grams, 3.74 moles
Trifluoroacetic anhydride, 297.6 grams, 1.42 moles.

The nonanoic acid was charged into a 2 litre flange pot equipped with an overhead stirrer, water condenser and addition inlet together with the trifluoroacetic anhydride. The resultant clear mixture was stirred up and heated to 100°C using a silicone oil bath and temperature probe. During heating it was noted that the colour of the reaction mixture darkened and developed a dark brown tinge. After allowing the mixture to stir for one hour at 100°C, the cellobiose was slowly added via a solid powder funnel to the dark activated solution, and a dirty brown suspension was formed which re-dissolved forming a clear black solution within 10-20 minutes.

The reaction flask was then maintained at 100°C for a total of 6 hours then cooled down to ambient laboratory temperature. Next the contents of the flask were transferred into 2 litres of methanol containing 10% de-ionised water in an ice-cooled 5 litre beaker. Immediately an off-white solid precipitate came out of solution, this was filtered off and collected. The crude solid was recrystallised a total of 4 times from a tetrahydrofuran/methanol solution producing a white solid product.

The product was obtained in a quantity of 31.5 g which was a 37% yield. It had a melting point of 110°C.

Step 2, partial de-acylation

Glacial acetic acid (2.04g) was added slowly dropwise with stirring into a solution of ethylenediamine (4.09g) in tetrahydrofuran (THF, 850cm^3). A white precipitate formed which remained during the reaction. α-Cellobiose octanonanoate (50g) was then added and the whole reaction mixture stirred at room temperature for a total of 48 hours.

At the end of the reaction period, the contents of the flask were transferred to a two litre separating funnel, 350cm^3 of water was added and the mixture extracted with dichloromethane (250cm^3). The organic layer was collected and further washed with successive 350cm^3 portions of (1) dilute HCl (0.1M), (2) aqueous sodium bicarbonate (1M) and (3) water.

The resultant organic phase was recovered, dried over anhydrous magnesium sulphate, filtered and the remaining solvent removed by rotary evaporation. A slightly sticky off-white crude solid was obtained. This was then re-crystallised from a mixture of THF/methanol (50:300cm^3). During overnight storage, a white solid precipitated out and was filtered off, dried and collected, yielding 30.5g of a white free-flowing solid as intermediate product (68% Yield).

Step 3.

3A - Re-acylation with an acyl chloride

This route is exemplified for the benzoate ester, and is useable for all the esters by substituting the other acid chlorides for benzoyl chloride.

A 3 neck 500cm^3 round bottomed flask was charged with cellobiose heptanonanoate (5g, 3.78x10^{-3}moles) together with 125cm^3 of toluene. The mixture was stirred thoroughly until a clear solution resulted. Next

triethylamine (0.479g, $4.73x10^{-3}$moles) was slowly added dropwise to the solution.

Thereafter, Benzoyl Chloride (0.665g, $4.73x10^{-3}$moles) was added slowly and cautiously via a pressure equalising dropping funnel into the reaction mix. When addition of the reagents was complete, the whole reaction solution was heated up to and maintained under reflux conditions for a total of 2-3hrs. The flask was then removed from the heat and after cooling was filtered to remove the solid triethylamine hydrochloride salt present. A clear straw coloured liquid was obtained. All solvent was then removed by rotary evaporation to give a crude product, a straw coloured gel-like material. The crude product was re-crystallised from THF-MeOH ($20cm^3$:$120cm^3$). The resultant product, a white free-flowing solid, was filtered off, collected and dried at 40-45°C. Yield was 3.5g (65%)

3B Re-acylation employing an acid/catalyst

This method is exemplified using benzoic acid and can also be used for making the other cellobiose esters by replacing benzoic acid by the appropriate acid.

A 2 neck $250cm^3$ round bottomed flask was charged with Benzoic Acid (29.54g, 0.24moles) and trifluoroacetic anhydride(19.05g, 0.091moles). The mixture was stirred and heated to and maintained at 100°C for one hour. Cellobiose heptanonanoate (5g, $3.78x10^{-3}$moles) was introduced slowly via a solids addition funnel into the activated solution. After it had added completely, the reaction mixture was maintained at 100°C stirred for a total of 6 hours. The reaction flask was then cooled down to room temperature. An ice-cooled solution of

methanol-water (400cm^3 MeOH:40cm^3 water) was poured into the flask, whereupon a solid precipitate formed immediately, was filtered off and re-crystallised from THF-MeOH (20cm^3:120cm^3). The resultant product was filtered off collected and re-crystallised a second time from THF-MeOH to remove trace acid. The final product, a white solid, was filtered off, collected and dried at 40-45°C. The yield was 3.1g (58%)

3C- Re-acylation using an anhydride

The method is exemplified using acetic anhydride and the other cellobiose esters can be made by substituting the appropriate anhydride for acetic anhydride.

A 3 neck 500cm^3 round bottomed flask was charged with cellobiose heptanonanoate (5g, 3.78x10^{-3}moles) and toluene (50 cm^3). The mixture was stirred, creating a pale yellow clear solution. Acetic anhydride (1.16g, 1.13x10^{-3}moles) was added slowly via a pressure equalising dropping funnel. When its addition was complete, the reaction mixture was heated up to 120°C and refluxed for 6hrs. The mixture was cooled down to room temperature and all solvent removed by rotary evaporation to yield a crude gel-like solid, which was filtered off and re-crystallised from THF-MeOH (20cm^3:120cm^3), filtered off, and dried at 40-45°C. Yield:- 4.4g (85%).

In Table 1, the substituent listed is at the anomeric carbon, and the %Y listed is the proportion of the anomeric OH which has been converted to the specified acyl group.

The %A (α anomer) and %Y (extent of acylation at the anomeric carbon) can be determined by ^{1}H NMR spectroscopy,

using a Bruker DRX 500MHz NMR Spectrometer. The samples were run in 99.8 atom % D-Chloroform (CDCl3) solvent containing 0.03% TetramethylSilane (TMS).

In the spectra obtained for acylated cellobiose using ^1H NMR spectroscopy, the alpha and the beta anomeric forms have distinct peaks at distinct chemical shifts. The location of the peaks also depends on whether the anomeric carbon is substituted by hydroxyl or by an acyl group. A doublet at low field is due to the proton on the anomeric carbon of the alpha-anomer ($J_{axial-equa}$= 3.8HZ; 6.26ppm) when the anomeric carbon has been acylated , whereas the corresponding doublet is at a chemical shift of 5.36ppm when its substituent is hydroxyl. Correspondingly, the spectrum comprises a set of doublets at a higher field due to the proton on the anomeric carbon of the beta anomer ($J_{axial-axial}$ 7.9HZ; 5.65 ppm) when the anomeric carbon is acylated and at a chemical shift of 4.82ppm when the anomeric carbon is merely hydroxyl substituted. A linear comparison of the peak areas enables the relative proportions of the two anomers to be determined.

The ability of ^1H NMR spectroscopy to distinguish between acylated cellobiose molecules in which the cellobiose anomeric carbon is substituted by an hydroxyl or acyl group can be enhanced by employing a method in which the spectrum of the as-made sample is taken, the hydroxyl group in the sample is reacted with trichloroacetyl isocyanate (TCAI) and the spectrum of the sample is taken again. The chemical shift for TCAI-adducted alpha molecule is 6.33ppm and for TCAI-adducted beta molecule is 5.73ppm. By comparing the peak areas of the spectra, the relative proportions of the alpha plus beta hydroxyl, alpha acylated, and beta acylated molecules can be determined.

Table 1

Ex No	Ester substituent	Route	α, β ratio	%Y	MP (°C)
1.1	Benzoyl	3A	2% α, 98% β	97	68
1.2	Benzoyl	3B	96% α, 4% β	100	85
1.3	2-Naphthoyl	3A	1% α, 99% β	100	84
1.4	2-Naphthoyl	3B	99% α, 1% β	100	85
1.5	Ethanoyl	3C	33% α, 67% β	98	68
1.6	Ethanoyl	3A	62% α, 38% β	99	87
1.7	Ethanoyl	3B	92% α, 8% β	79	92
1.8	n-Hexadecanoyl	3A	16% α, 84% β	97	50
1.9	n-Hexadecanoyl	3B	98% α, 2% β	100	55
1.10	Cyclohexanoyl	3A	3% α, 97% β	100	79
1.11	Cyclohexanoyl	3B	89% α, 11% β	97	70

n-Propanoyl, n-Butanoyl-, n-Octanoyl-, n-Decanoyl- and biphenoyl esters at the anomeric carbon of cellobiose heptanonanoate can similarly be made by step 3A or step 3B.

Example 2

In this Example, cellobiose heptadecanoate esters are prepared using the routes described for Example 1, but employing decanoic acid instead of nonanoic acid in step 1. The results are summarised in Table 2 below.

Table 2

Ex No	Ester substituent	Route	α, β ratio	%Y	MP (°C)
2.1	Benzoyl	3A	4% α, 96% β	100	79
2.2	Benzoyl	3B	82% α, 18% β	93	85
2.3	Ethanoyl	3C	38% α, 62% β	94	77
2.4	Ethanoyl	3A	59% α, 41%β	98	87
2.5	Ethanoyl	3B	95% α, 5% β	86	102

The corresponding 2-Naphthoyl, and hexadecanoyl esters can be made using routes 3A or 3B.

Cellobiose octanonanoate, cellobiose octadecanoate and cellobiose heptanonaoate reference materials

Ref	Acyl Groups	α, β ratio	%Y	MP (°C)
R1	Nonanoyl	100% α,	100	97
R2	Nonanoyl	88% α, 12% β	98	80
R3	Nonanoyl	99 β	100	80
R4	Decanoyl	85% α, 15%β	84	85
R5	Nonanoyl	50% α, 50% β	0	114
R6	Decanoyl	50% α, 50% β	0	105

Example 3.

In this Example, samples of esterified cellobiose prepared as in Example 1 or 2 above, were used to gel water-immiscible cosmetic liquids, in accordance with the procedure given below, in which a large number of gels can be prepared simultaneously.

The samples were tested in a 96 well (8 x 12 rows) glass micro-titre plate. Each well had a volume of about 1ml. About 0.01 or 0.02g of each esterified cellobiose material was placed into 8 consecutive wells in a single row, so that each well contained approximately 5% or 10% of the cellobiose ester. The balance in each well comprised the cosmetic liquid by addition of approximately 0.2g of the respective liquid to each cell. A glass lid was placed on top of the plate. The plate was carefully placed in a thermostatically controlled fan-assisted oven set at 150°C for 2.5 hours. The plate was removed from the oven and allowed to cool naturally to ambient laboratory temperature. The contents of the wells were assessed at the end of the cooling period, by visual inspection and by poking the contents of each well with a micro-spatula. The plates were stored at 18°C for 18 hours and the contents inspected, and further stored for 18 hours at 4°C and inspected for a third time. The results obtained in the tests are summarised in the Tables below.

Table 3

Product of Ex 1.1	5%	10%
ISA	gel after 18hrs at 22°C	gel
IPM	gel after 18 hrs at 4°C	gel
Mineral oil	gel	gel
Finsolv TN	gel after 18hrs at 4°C	gel
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 4

Product of Ex 1.2	5%	10%
ISA	soft gel	gel
Mineral oil	soft gel	gel
Fluid AP	soft gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 5

Product of Ex 1.3	5%	10%
ISA	gel	gel
IPM	gel after 18hrs at 4°C	gel after 18hrs at 22°C
Mineral oil	gel after 18hrs at 22°C	gel after 18hrs at 22°C
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 6

Product of Ex 1.4	5%	10%
ISA	gel after 18 hrs at 22°C	gel after 18hrs at 22°C
Mineral oil	gel after 18 hrs at 22°C	gel after 18hrs at 22°C
Fluid AP	gel	gel
Polydecene	gel after 18 hrs at 22°C	gel
DC556	gel	gel

Table 7

product of Ex 1.5	5%	10%
ISA	gel after 18 hrs at 22°C	gel
Mineral oil	soft gel after 18hrs at 22°C	gel
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel after 18 hrs at 22°C	gel

Table 8

Product of Ex 1.6	5%	10%
ISA	soft gel	gel
Mineral oil	soft gel	gel
Fluid AP	soft gel	gel
Polydecene	gel	gel
DC556	soft gel after 18hrs at 22°C	gel

Table 9

Product of Ex 1.7	5%	10%
ISA	soft gel	gel
Mineral oil	soft gel	gel
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 10

Product of Ex 1.8	5%	10%
ISA	gel after 18 hrs at 22°C	gel after 18 hrs at 22°C
Mineral oil	gel after 18 hrs at 22°C	gel after 18 hrs at 22°C
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 11

Product of Ex 1.9	5%	10%
ISA	gel after 18 hrs at 22°C	gel after 18 hrs at 22°C
IPM	gel after 18 hrs at 4°C	gel after 18 hrs at 4°C
Mineral oil	gel after 18 hrs at 22°C	gel after 18 hrs at 22°C
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 12

Product of Ex 1.10	5%	10%
ISA	gel after 18 hrs at 22°C	gel
Mineral oil	gel	gel
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 13

Product of Ex 1.11	5%	10%
ISA	gel after 18 hrs at 22°C	gel after 18 hrs at 22°C
Mineral oil	gel after 18 hrs at 22C	gel after 18 hrs at 22°C
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel after 18 hrs at 22°C	gel

Table 14

Product of Ex 2.1	5%	10%
ISA	gel	gel
IPM	solution	gel after 18hrs at 22°C
Finsolv TN	solution	gel after 18hrs at 22°C
Mineral oil	gel	gel
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 15

Product of Ex 2.2	5%	10%
ISA	gel	gel
Mineral oil	gel	gel
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 16

Product of Ex 2.3	5%	10%
ISA	gel	gel
Mineral oil	gel	gel
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 17

Product of Ex 2.4	5%	10%
ISA	gel	gel
Mineral oil	gel	gel
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Table 18

Product of Ex 2.5	5%	10%
ISA	gel	gel
IPM	solution	gel after 18 hrs at 22°C
Finsolv TN	solution	gel after 18 hrs at 22°C
Mineral oil	gel	gel
Fluid AP	gel	gel
Polydecene	gel	gel
DC556	gel	gel

Example 4

In this Example the Fibre dissolution temperature (FDT) is measured in the DSC process described later herein, by observing when the fibres dissolve whilst the temperature of sample rises. FDT is taken to be the peak temperature of the highest peak.

The results are summarised in Table 19 below in which Anomeric description indicates the α:β ratio and the acyl substituent at the anomeric carbon

Table 19

Code	Product of	Anomeric Description	FDT (°C)	Solubility of structurant at 25°C
R2		nonanoyl, 88% α	47	Benchmark. Some dissolution of structurant clearly seen in DSC
R3		nonanoyl, 99% β	47	Slightly less soluble than benchmark. Some dissolution of structurant seen in DSC
Ex 4.1	Ex 1.1	benzoyl, 98% β	64	Less soluble. No dissolution of fibres seen in DSC
Ex 4.2	Ex 1.2	benzoyl, 96% α	67	Less soluble. No dissolution of fibres seen in DSC
Ex 4.3	Ex 1.3	naphthoyl, 99% β	63	Less soluble. No dissolution of fibres seen in DSC
Ex 4.4	Ex 1.5	ethanoyl, 33% α	50	Less soluble. No dissolution of fibres seen in DSC
Ex 4.5	Ex 1.6	ethanoyl, 62% α	70	Less soluble. No dissolution of fibres seen in DSC
Ex 4.6	Ex 1.7	ethanoyl, 92% α	72	Less soluble. No dissolution of fibres

				seen in DSC
Ex 4.7	Ex 1.10	cyclohexanoyl, 97% β	55	Less soluble. No dissolution of fibres seen in DSC

From Table 19, two deductions can be made. First, the fibre dissolution temperature of the structurants according to the instant invention are higher than the reference structurants, indicating that the thermal stability (stability to melting) of a gel obtained using that structurant is higher.

Secondly, the solubility of the invention structurants at 25°C tends to be lower than that of the reference structurants, which we have found indicates that their resistance to crystallisation during storage is improved.

DSC Method

About 20 mg samples of gel were sealed in stainless steel capsules for DSC. An empty stainless steel capsule was used as the physical reference. The samples were subjected to the following temperature programme:

The sample was heated to 100°C and held at 100°C for 1 minute, in order to obtain an isotropic solution. The sample was then cooled at 5 K/min to -20°C. The sample was held at -20°C for 1 minute. The sample is now a gel on the bottom of the sample capsule prepared in a reproducible manner. The gel was then heated at 5 K/min to 100°C. Data was also obtained with empty stainless steel pans as both physical sample and reference. This blank data was later subtracted from the sample data to remove any curvature in the base line.

Example 5

Stability Testing

Gels were made up using 10% structurant in a 60:40 mixture of Hydrogenated Polyisobutene (Panalene L14E):DC245. The gels, in sealed glass bottles, were left to stand for 18hrs at room temperature, after which they were transferred to an oven thermostatically controlled to 37°C. Samples were checked periodically for signs of crystal growth visible by eye. The results are summarised in Table 20 below

Table 20

Structurant	Observation
R1	◦ Small crystals visible in gel after 18hrs at RT. ◦ More and bigger crystals after 6hrs at 37°C. ◦ Crystals throughout gel after 3 days at 37°C.
R2	◦ Slight loss of clarity after 7 days at 37 °C. ◦ Fine crystals on surface after 8 days at 37 °C. ◦ Fine needle crystals throughout gel after 9 days at 37 °C. ◦ More needle crystals in gel bulk and crystal mass on surface after 13 days at 37 °C. ◦ Large amount of crystals throughout

	gel after 17 days at 37 °C.
Product of Ex 1.7	No crystals after 17 days.
Product of Ex 1.2	No crystals after 17 days.
Product of Ex 1.10	No crystals after 17 days.

Table 20 shows that there is a distinct advantage for the invention structurants over both R1 and R2 in terms of resistance to crystallisation during storage.

Example 6

This Example shows some benefits obtainable by employing a fraction of a structurant in accordance with the present invention in conjunction with a structurant exemplified or described in PCT/GB 00/01228.

In this Example, 60:40 polydecene:DC245 was gelled with a combination of 9 % cellobiose octanonanoate (87.5% α, code R2) and 1% of the specified cellobiose ester. The transparency and light transmission of the samples are summarised in Table 21, in which %T is the % light transmitted at a wavelength of 580nm.

Table 21

	Code	Anomeric Description	Clarity	
			Visual	% T
R2		nonanoyl, 87.5% α	transparent/ slight haze 5	41
R3		nonanoyl, 99% β	transparent/ translucent 4	46
R5		hydroxy, 50% α	transparent/ translucent 4	31
Ex 6.1	Ex 1.1	benzoate, 98% β	transparent/ translucent 5	55
Ex 6.2	Ex 1.2	benzoate, 96% α	transparent/ translucent 4	38
Ex 6.3	Ex 1.3	naphthaloate, 99%β	transparent 4	58
Ex 6.4	Ex 1.4	naphthaloate, 99%α	transparent/ sight haze >8	38
Ex 6.5	Ex 1.5	ethanoate, 33% α	transparent >8	49
Ex 6.6	Ex 1.6	ethanoate, 62% α	transparent >8	49
Ex 6.7	Ex 1.7	ethanoate, 92% α	transparent >8	52
Ex 6.8	Ex 1.9	hexadecanoate, 98% α	transparent >8	45
Ex 6.9	Ex 1.10	cyclohexanoate, 97% α	transparent/ slight haze 6	42

From Table 21, it can be seen that the addition of the invention structurants tended to produce a gel that was visually a little better in that the panel score was higher than when the reference structurants were added. This is confirmed by the %T data, light transmission,

which similarly showed a similar and for most, a higher light transmission.

Visual assessment score. A gel contained within a 1cm thick cuvette was placed directly on to a sheet of white paper on which 21 sets of figures where printed in black. The size and thickness of the figures varied systematically and were numbered from -12 (the largest, thickest set) through 0 to 8 (the smallest thinnest set) The score given to each gel was the highest numbered set which could be read clearly through the gel, the higher the number, the higher the clarity.

Light transmission

The translucency of a composition may be measured by placing a sample of standardised thickness in the light path of a spectrophotometer and measuring transmittence, as a percentage of light transmitted in the absence of the gel.

This test was carried out using a dual-beam spectrophotometer. The sample of composition was poured hot into a 4.5 ml cuvette made of poly(methyl-methacrylate) (PMMA) and allowed to cool to an ambient temperature of 20-25°C. Such a cuvette gives a 1 cm thickness of composition. Measurement was carried out at 580 nm, with an identical but empty cuvette in the reference beam of the spectrophotometer, after the sample in the cuvette had been held for 24 hours. A transmittence measured at any temperature in the range from 20-25°C is usually adequately accurate, but measurement is made at 22°C if more precision is required.

Example 7

In this Example, the procedure of Example 6 was followed, but employing 9% R4 to which was added 1% of itself or the other reference or invention material. The gels were tested in the same manner as in Example 6 and the results summarised in Table 22 below.

Table 22

	Product of	Anomeric Description	Clarity	
			Visual	% T
R4		decanoyl, 85% α	opaque <-12	0.36
R6		hydroxyl, 50% α	opaque <-12	0.8
Ex 7.1	Ex 2.1	benzoate, 96% β	translucent -1	9.53

From Table 22, it can be seen that the addition of the invention structurants tended to produce a gel that was visually much better in that the panel score was higher than when the reference structurants were added. This is confirmed by the %T data, light transmission, which similarly showed a much higher light transmission.

Example 8

Stability Testing

Gels were made up and tested in accordance with the procedure in Example 5, as such or modified by employing a weight ratio of 9% of R1 and 1% of an additional structurant as specified in Table 23 below.

Table 23

Structurant	Observation
solely R1	Small crystals visible in gel after 18 hrs at RT. More and bigger crystals after 6 hrs at 37°C. Crystals throughout gel after 3 days at 37°C.
+ R3	Some crystal growth on gel surface after 1 day at 37°C. Much more crystallisation at surface and needle shaped crystals in bulk gel after 6 days at 37°C. Crystals throughout gel after 9 days at 37 °C More crystals throughout gel after 13 days at 37°C.
the product of Ex 1.1	Slight crystal growth on surface after 11 days at 37 °C.
the product of Ex 1.3,	No crystals after 12 days at 37 °C.
the product of Ex 1.7	Slight crystal growth on surface after 13 days at 37 °C.
the product of Ex 1.8	No crystals after 15 days at 37 °C.
the product of Ex 1.10	No crystal growth after 12 days at 37 °C.

Table 23 shows that there is significant improvement in stability as a result of adding a proportion of the structurant of the instant invention to the structurant

of PCT/GB 00/01228. Likewise there is a benefit for adding the invention products compared with adding reference product R3 to the structurant of PCT/GB 00/01228.

Example 9

The test procedure of Example 8 was repeated, but using reference structurant R2 as the structurant to which the invention and reference structurants were added. The results are summarised in Table 24 below.

Table 24

Structurant	Observation
solely R2	Slight loss of clarity after 7 days at 37 °C. Fine crystals on surface after 8 days at 37 °C. Fine needle crystals throughout gel after 9 days at 37 °C. More needle crystals in gel bulk and crystal mass on surface after 13 days at 37 °C.
product of Ex 1.1	No crystals after 12 days at 37 °C.
product of Ex 1.3	No crystals after 12 days at 37 °C.
product of Ex 1.7	Slight very fine crystal growth after 13 days at 37 °C.
product of Ex 1.10	Some needle crystals on surface after 11 days at 37 °C. Some needle crystals in gel bulk after 12 days at 37 °C.

From Table 24, it can be seen that the addition of the invention structurants to reference structurant R2 according to PCT/GB 00/1228 improves the resistance of the structurant to crystallisation during storage.

Example 10

An antiperspirant suspension stick was prepared using a water-immiscible liquid or a mixture of water-immiscible liquids, an antiperspirant active and an esterified cellobiose. The procedure was as follows:
the mixture of liquids was heated to a temperature 5 to 10°C above a temperature at which the esterified cellobiose had been observed to dissolve in a preliminary test. During this heating the liquid was mixed gently using a Silverson mixer. The esterified cellobiose was added and allowed to dissolve. Next, the particulate antiperspirant active was added to this solution. The resulting mixture was then allowed to cool (or, if necessary, heated) whilst mixing gently until it reached a temperature of about 5 to 10° above the gelling point. At this stage the mixture was poured into antiperspirant stick barrels and left to cool without further disturbance until the formulation had solidified.

The resulting sticks were evaluated after at least 24 hours at ambient laboratory temperature, the appearance of the stick was noted, the hardness was determined by penetrometer, and tests of deposition and whiteness of the resulting deposit were carried out using the procedures described hereinafter. The results are summarised in Table 25 below.

Table 25

Constituent	% w/w
Al/Zr Tetrachlorohydrex glycine complex (AZAG)	24.0
Silkflo 364NF (Polydecene)	13.8
DC245 (volatile silicone)	55.2
Cellobiose octanonanoate (R1)	6.3
Ester prepared in Ex 1.7	0.7
Penetrometer Hardness (mm)	14.6
Deposition on black wool after 24 hours	33

From Table 25, it can be seen that a suspension stick with suitable hardness and low visible deposition can be made using a combination of the cellobiose structurant according to PCT/GB 00/01228 and the invention structurant.

Further suspension sticks having acceptable hardness and low visible deposits can be made by substituting the structurant made in each of Examples 1.1 to 1.6 or 1.8 to 1.11 for that made in Ex 1.7 or for the combined weight of R1 plus that of Ex1.1 in the above formulation or similarly for 2.1 to 2.5 in combination with R4 instead of R1.-

Example 11

In this Example, an emulsion stick was prepared by mixing cyclomethicone with the other organic liquids including the cetyl dimethicone copolyol which functioned as an

emulsifier (silicone surfactant) and the mixture was heated with gentle stirring to a temperature 5 to 10°C above the temperature at which the structurant had been found to dissolve. The esterified cellobiose was then added and allowed to dissolve.

The disperse phase (also referred to as internal phase) was an aluminium zirconium active dissolved in water or in a mixture of a polyol and water. This disperse phase was pre-heated to the same temperature as the organic oils containing the esterified cellobiose and added slowly to them over a period of one minute while mixing with a Silverson mixer. After addition was complete the formulation was mixed at higher speed for five minutes. Stirring speed was then reduced for a further one minute after which the mixture was poured into stick barrels and allowed to cool undisturbed to ambient laboratory temperature. The sticks were tested by penetrometer, and for whiteness of deposits, in each instance by the test procedures given earlier. The results are summarised in Table 26 below.

Table 26

Constituent	% w/w
Zirconal 50 (50% aqueous solution of Al/Zr Tetrachlorohydrex glycine complex)	40.0
Glycerol	10.0
Silkflo 364NF (Polydecene)	25.52
DC245 (volatile silicone)	18.48
ABIL EM90 (emulsifier - silicone copolymer)	1
Ester prepared in Ex 1.10	5.0

Penetrometer Hardness (mm)	17.1
Deposition on black wool after 24 hours	17
% Light Transmission at 580nm at 19°C	34

From Table 26, it can be seen that the emulsion stick produced according to Example 11 had acceptable hardness and particularly low visible deposits and has high visual clarity.

Further emulsion sticks having acceptable hardness and low visible deposits are made by substituting the structurant made in each of Examples 1.1 to 1.9 or 1.11 or 2.1 to 2.5 for that made in Ex 1.10 or by substituting up to 90% of the weight of the structurant by R1 or R2 or R4 described hereinabove.-

Measurement of Properties

Hardness of stick using a penetrometer
The hardness and rigidity of a composition which is a firm solid can be determined by penetrometry. If the composition is a softer solid, this will be observed as a substantial lack of any resistance to the penetrometer probe.

A suitable procedure is to utilises a lab plant PNT penetrometer equipped with a Seta wax needle (weight 2.5 grams) which has a cone angle at the point of the needle specified to be 9°10′ ± 15′. A sample of the composition with a flat upper surface is used. The needle is lowered onto the surface of the composition and then a penetration hardness measurement is conducted by allowing the needle with its holder to drop under a total weight,

(i.e. the combined weight of needle and holder) of 50 grams for a period of five seconds after which the depth of penetration is noted. Desirably the test is carried out at a number of points on each sample and the results are averaged. Utilising a test of this nature, an appropriate hardness for use in an open-ended dispensing container is a penetration of less than 30 mm in this test, for example in a range from 2 to 30 mm. Preferably the penetration is in a range from 5mm to 20 mm.

In a specific protocol for this test measurements on a stick were performed in the stick barrel. The stick was wound up to project from the open end of the barrel, and then cut off to leave a flat, uniform surface. The needle was carefully lowered to the stick surface, and then a penetration hardness measurement was conducted. This process was carried out at six different points on the stick surface. The hardness reading quoted is the average value of the 6 measurements.

Deposition and whiteness of deposit

Another test of the properties of a composition is the amount of the composition which is delivered onto a surface when the composition is drawn across that surface (representing the application of a stick product to human skin). To carry out this test of deposition, a sample of the composition with standardised shape and size is fitted to apparatus which draws the sample across a test surface under standardised conditions. The amount transferred to the surface is determined as an increase in the weight of the substrate to which it is applied. If desired the colour, opacity or clarity of the deposit may subsequently be determined.

A specific procedure for such tests used apparatus to apply a deposit from a stick onto a substrate under standardised conditions and then measures the mean level of white deposits using image analysis.

The substrate used was
12 x 28cm strip of black Worsted wool fabric.

The substrates were weighed before use. The sticks were previously unused and with domed top surface unaltered.

The apparatus comprised a flat base to which a flat substrate was attached by a clip at each end. A pillar having a mounting to receive a standard size stick barrel was mounted on an arm that was moveable horizontally across the substrate by means of a pneumatic piston.

Each stick was kept at ambient laboratory temperature overnight before the measurement was made. The stick was advanced to project a measured amount from the barrel. The barrel was then placed in the apparatus and a spring was positioned to biased the stick against the substrate with a standardised force. The apparatus was operated to pass the stick laterally across the substrate eight times. The substrate was carefully removed from the rig and reweighed.

Whiteness of Deposit

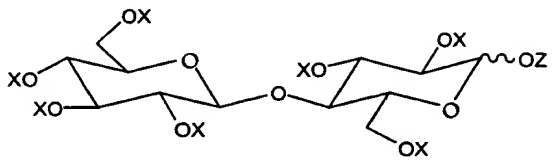
The deposits from the previous test were assessed for their whiteness after an interval of 24 hours approximately.

This was done using a Sony XC77 monochrome video camera with a Cosmicar 16mm focal length lens positioned vertically above a black table illuminated from a high angle using fluorescent tubes to remove shadowing. The apparatus was initially calibrated using a reference grey card, after the fluorescent tubes had been turned on for long enough to give a steady light output. A cloth with a deposit thereon from the previous test was placed on the table and the camera was used to capture an image. An area of the image of the deposit was selected and analysed using a Kontron IBAS image analyser. This notionally divided the image into a large array of pixels

and measured the grey level of each pixel on a scale of 0 (black) to 255 (white). The average of the grey intensity was calculated. This was a measure of the whiteness of the deposit, with higher numbers indicating a whiter deposit. It was assumed that low numbers show a clear deposit allowing the substrate colour to be seen.

Claims

1 As a new compound, an acylated cellobiose satisfying the general formula:



in which X represents an acyl group -R-CO- or H, Z represents an acyl group R'-CO- or H and not more than a minority of R + R' residues represent H and in the remaining R + R' residues, R represents a saturated or unsaturated, linear or branched chain hydrocarbon residue containing from 5 to 31 carbon atoms and

R' represents a residue which is different from R and which is :-

(i) a saturated or unsaturated, linear or branched chain hydrocarbon residue containing from 1 to 31 carbon atoms optionally substituted or (ii) an aromatic hydrocarbon residue, optionally substituted or (iii) a cycloaliphatic hydrocarbon, optionally substituted.

2 An acylated cellobiose according to claim 1 characterised in that each X represents a R-CO- group.

3 An acylated cellobiose according to claim 1 or 2 characterised in that the R residues are the same.

4 An acylated cellobiose according to any preceding claim characterised in that the R residue is linear.

5 An acylated cellobiose according to any preceding claim characterised in that the R residue comprises from 7 to 11 and preferably 8 or 9 carbons.

6 An acylated cellobiose according to any preceding claim characterised in that the R residue is n-octyl or n-nonyl.

7 An acylated cellobiose according to any preceding claim characterised in that the R' residue is an alkyl residue containing from 1 to 6 or from 11 to 24 carbon atoms, optionally substituted.

8 An acylated cellobiose according to any preceding claim characterised in that the R' residue is a linear alkyl residue.

9 An acylated cellobiose according to any of claims 1 to 6 characterised in that the R' residue comprises a phenyl, naphthyl or biphenyl residue.

10 An acylated cellobiose according to any of claims 1 to 6 characterised in that the R' residue comprises a cycloalkyl residue and preferably a cyclohexyl or cyclooctyl residue.

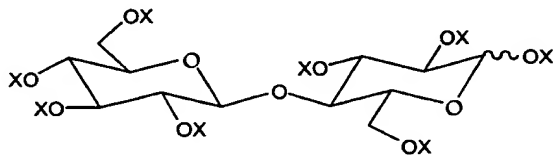
11 An acylated cellobiose according to any preceding claim characterised in that the major fraction and preferably at least 90% of the acylated cellobiose is the α anomer.

12 An acylated cellobiose according to any of claims 1 to 10 characterised in that the major fraction and preferably at least 90% of the acylated cellobiose is the β anomer.

13 An acylated cellobiose according to any preceding claim characterised in that not more than 50% and preferably not more than 25% of the Z residue represents H.

14 An acylated cellobiose according to claim 1 which is selected from cellobiose heptanonanoate benzoate, cellobiose heptanonanoate naphthanoate, cellobiose heptanonanoate ethanoate, and cellobiose heptanonanoate cyclohexanoate and cellobiose hepta(decanoate) benzoate.

15 A method for preparing an acylated cellobiose according to claim 1 comprising the step of reacting an acylated cellobiose having general formula 2



in which X represents an acyl group (R-CO-) or H, being not more than a minority of X residues and R represents a saturated or unsaturated, linear or branched chain hydrocarbon residue containing from 5 to 31 carbon atoms with an acylating agent containing a residue R′ as described in claim 1

preferentially at the anomeric carbon of the cellobiose.

16 A method according to claim 15 characterised first reacting cellobiose with an acylating agent containing a residue R as described in claim 1 in an amount such that a majority of hydroxyl substituents in the cellobiose are acylated, including the hydroxyl group at its anomeric carbon atom,

secondly, at least partially deacylating the product of the first step at the anomeric carbon in the cellobiose and

thereafter in a third step reacting the product of the second step with an acylating agent containing the residue R'.

17 A method according to claim 14 characterised in that the acylating agent employed for acylating at the anomeric carbon is an acid chloride or carboxylic acid anhydride or carboxylic acid/strong acid anhydride catalyst.

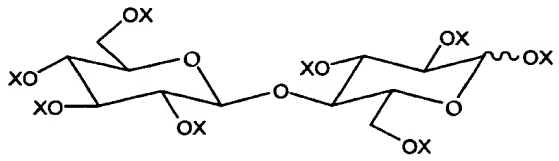
18 A method of thickening or structuring a water-immiscible liquid to form a cream, soft solid or solid comprising the steps of forming a solution of a gellant in the water-immiscible liquid at a temperature above its gelling temperature and thereafter cooling the solution to and maintaining it at below its gelling temperature until its viscosity has increased or until it has solidified characterised in that the gellant comprises an acylated cellobiose as specified in any of claims 1 to 14.

19 A cream, soft solid or solid composition comprising a water-immiscible liquid structured or thickened by an effective amount of a gellant in which the gellant comprises an acylated cellobiose as specified in any of claims 1 to 14.

20 A composition according to claim 19 which contains the gellant in an amount selected in the range of from 0.1 to 20% and particularly from 0.5 to 15% by weight of its combined weight with the water-immiscible liquid.

21 A composition according to claim 19 or 20 in which said acylated cellobiose represents a major fraction of the gellant.

22 A composition according to claim 19 or 20 in which said acylated cellobiose is employed in conjunction with a gellant (ACB) that is represented by the formula



in which X represents an acyl group (R-CO-) or H, being not more than a minority of X residues and R represents a saturated or unsaturated, linear or branched chain hydrocarbon residue containing from 5 to 31 carbon atoms.

23 A composition according to claim 22 in which said acylated cellobiose is employed in a weight ratio to

said ACB of from 25:1 to 1:25, preferably from 1:1 to 1:12.

24 A composition according to any of claims 19 to 23 which additionally contains one or more active agents selected from skin benefit agents, personal care agents, medicaments, sunscreen or tanning aid.

25 A composition according to claim 24 in which said personal care agent comprises an antiperspirant or a deodorant.

26 A composition according to any of claims 19 to 25 in which the active agent is dissolved or suspended in the water-immiscible liquid.

27 A composition according to any one of claims 19 to 26 in which the thickened or structured water-immiscible liquid forms an emulsion or micro-emulsion with an aqueous or water-miscible liquid.

28 A composition according to claim 27 in which the or an active agent is dissolved in the aqueous or water-miscible liquid.

29 A composition according to claim 25, 27 or 28 in which the or an active agent comprises an antiperspirant salt.

30 A composition according to claim 29 in which the antiperspirant salt comprises an aluminium salt or an aluminium and zirconium salt, preferably selected

from aluminium chlorohydrate, aluminium/zirconium chlorohydrate and a complex of aluminium and zirconium chlorohydrate with glycine.

31 A composition according to any of claims 27 to 30 in which the emulsion is a water-in-oil emulsion.

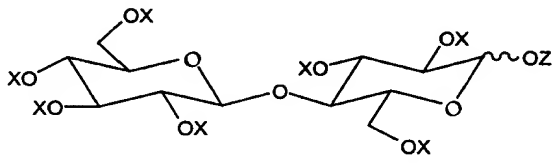
32 A composition according to claim 31 which is transparent or translucent and is preferably a transparent or translucent stick.

33 Cosmetic use of a composition according to any of claims 18 to 32in which the composition is applied topically to skin.

Abstract

Esters

Acylated cellobiose compounds exhibiting a desirable combination of properties are provided which satisfy the formula;-



in which X represents an acyl group (R-CO-) or H, Z represents an acyl group (R'-CO-) or H and not more than a minority of X + Z residues represent H,

R represents a saturated or unsaturated, linear or branched chain hydrocarbon residue containing from 5 to 31 carbon atoms and

R' represents a residue which is different from R and which is :-

(i) a saturated or unsaturated, linear or branched chain hydrocarbon residue containing from 1 to 31 carbon atoms, optionally substituted or (ii) an aromatic hydrocarbon residue, optionally substituted or (iii) a cycloaliphatic hydrocarbon, optionally substituted.

These acylated cellobiose compounds are particularly suited to thickening or structuring a water-immiscible liquid, for example when such a liquid provides a phase in a cosmetic formulation, and especially antiperspirant or deodorant formulations. Especially desirable formulations comprise water in oil emulsions, and particularly those which are transparent or translucent